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The Mathematical Model of the Adsorption of Some Anions on MnO_2

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Abstract

Mathematical models were obtained to predict the adsorption of some anions on MnO_2 in a leclanche dry cell from interpolated data obtained from preview experimental work. The models obtained were linear, non-linear, and non-linear with interaction. Polymat 3 and FORTRAN-77 programs were used to simulate the models.

The divalent ions absorption emerged the best in the study. It had a consistent order of decreasing surface charge from 1M to 0.001M solutions and has the highest R^2. Likewise the R^2 of monovalent was 0.47, and 0.49 for combined monovalent and divalent ions.

Keywords: *Leclanche dry cell, interpolated data**,** Polymat 3 and FORTRAN-77 programs, monovalent, divalent ions**.***

Introduction

Modeling is an art of establishing interrelationship between important entities of a system (Drago *et al.* 1985; Anon. 1980). Mathematical model is a mathematical representation of a physical system, in which the variables are assigned values and the relationships between the variables are expressed in corresponding mathematical form (Anon. 1980). For the adsorption of anions on MnO_2, static mathematical models would be considered. The relationship between concentration of anions, pH of anion solution and adsorption can be expressed by algebraic equations (Aloko 2002).

Simulation is the technique of constructing and running a model of a real system in order to study its behavior without disrupting the environment of the system. Computer simulation involves the running of a special program on a suitable type of computer that generates time responses of the model that imitate the behavior of the process being studied. This work made use of digital simulation using FORTRAN-77 language. For every simulation, the following procedure is considered: data collection, problem analysis, simulation model specification, model programming, simulation experimentation, evaluation and interpretation of simulation results, and report concentration.

An electrochemical (Galvanic) cell is a device that can undergo a chemical reaction with the production of electrical energy during the process (Kubasov *et al.* 1987; Abbort 1984). Concisely, lechlanche cell is a type of Galvanic cell of the first order, that is, a primary cell (Wingrave *et al.* 2001).

The general chemical reaction-taking place in a leclanche dry cell is as follows (Bockris *et al.* 1998):

$$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3, \quad (1)$$

$$Zn + 2NH_4Cl \rightarrow ZnCl_2 + 2NH_3 + H_2. \quad (2)$$

The hydrogen gas produced from Equation (2) above seriously reduces the efficiency of the dry cell in two ways:

1. It increases the electrical resistance of the system.
2. It forms a back Electromotive force(E.M.F.) with zinc cathode

The two effects combined to reduce the life span of a lechlanche dry cell (Tomilov 1984).

The manganese dioxide in the cell serves to minimize the first effect by depolar-izing H_2 formation as given in Equation (3).

$$H_2 + 2MnO_2 \rightarrow H_2O + MnO_2 \qquad (3)$$

While the addition of alkaline or alkaline earth anions to the manganese dioxide greatly reduced the second effect (Wingrave 2001).

The anions can either combine with zinc to minimize back Electromotive force (E.M.F.) or combined with hydrogen to minimize polarization (Antropov 2002). Experiments carried out to ascertain this observation involved the study of adsorption of anions on MnO_2 in the cell.

It is on this basis that mathematical models were developed to explain the adsorption of these anions on MnO_2 and a simulation program of the models were obtained to:

1. Predict the extent of adsorption of anions on MnO_2 in a dry cell.
2. Finally, the models were tested using data obtained from previous experiments on adsorption of anions on MnO_2 in dry cell.

Experimental Methodology

Potentiometric Titration

The method of potentiometer titration was used to obtain the adsorption of the investigated anions (NO_3^-, Cl^-, Br^-, SO_4^{2-}) on MnO_2 decreasing from 1M to 0.001M of their sodium salts (Aloko 2002).

From results of the experiments, the change in volume (difference between the volume of anion without MnO_2 and with MnO_2) was determined, and by method of interpolation the adsorption (θ) and surface charge was then calculated.

Table 1 shows the Interpolation Values Obtained from Potentiometric Titration experiment in the study of adsorption of some anions on MnO_2 in the cell (Bamidele 2003).

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Mathematical Model of the System

Basis: The model was based on law of conservation of mass. That is to say the amount of anions adsorbed on MnO_2 is equal to the amount of anions present in the system.

Assumption: The following assumptions were made in developing mathematical equation for the adsorption of the anions on MnO_2 used in the dry cell:

(1) The amount of anions deposited (adsorbed) will not be smaller than expected but will be equal to the quantity of electricity required, i.e. no side reaction (deviation from Faraday's law).

(2) No partial dissolution of the products (adsorbed anion) deposited at the electrode, neither their oxidation at their electrodes nor the like, due to secondary reaction.

The proposed mathematical models due to static interaction of the factors that are algebraic in nature are of three types:

1. Linear ordinary differential equation in the form:

$$\theta = a_0 + a_1x_1 + a_2x_2 \qquad (4)$$

2. Non-linear ordinary differential equation in the form:

$$\text{Log } \theta = a_0 + a_1\log x_1 + a_2\log x_2 \qquad (5)$$

3. Non-linear ordinary differential equation in the form:

$$\theta = a_0 + a_1x_1 + a_2x_2 + a_3x_1.x_2 \qquad (6)$$

where θ = adsorption, x_1 = concentration of additive and x_2 = concentration of electrolyte. Tables 2, 3, and 4 include the mathematical modeled equations of monovalent ions, divalent ions, and combined monovalent and divalent ions.

Table1. The Effect of Concentration of Additives on Adsorption.

		NO_3^-		Br^-		Cl^-		SO_4^{2-}	
Concentration of additive	PH	ΔV	$\theta x10^{-12}$	ΔV	$\theta x10^{-12}$	ΔV	$\theta x10^{-12}$	ΔV	$\theta x10^{-12}$
x_1	x_2								
1	8.5	1.59	9.242	1.09	6.340	1.19	6.921	1.49	8.666
1	9.0	1.61	9.364	1.20	6.987	1.22	7.096	1.66	9.685
1	9.5	1.77	10.295	1.33	7.736	1.34	7.794	1.83	10.644
1	10.0	2.00	11.633	1.47	8.557	1.47	8.550	2.02	11.749
1	10.5	2.10	12.214	1.21	7.038	1.74	10.120	2.35	13.668
1	11.0	2.41	14.017	0.92	9.351	2.32	13.494	3.08	17.914
0.1	8.5	0.85	4.944	1.03	5.991	1.50	8.724	0.82	4.769
0.1	9.0	0.78	4.537	1.08	6.282	1.57	9.132	0.87	5.060
0.1	9.5	0.72	4.188	1.14	6.631	1.65	9.597	0.93	5.409
0.1	10.0	0.97	5.643	1.38	8.026	1.75	10.062	0.99	5.758
0.1	10.5	1.10	6.398	1.75	10.182	1.85	10.760	1.08	6.282
0.1	11.0	1.10	6.863	2.16	12.558	1.97	11.458	1.24	7.212
0.01	8.5	0.93	5.409	0.67	3.897	0.70	4.071	0.78	4.537
0.01	9.0	1.01	5.874	0.70	4.071	0.70	4.071	0.81	4.711
0.01	9.5	1.21	7.038	0.85	4.944	0.72	4.188	0.90	5.235
0.01	10.0	1.55	9.015	1.01	5.874	0.74	4.304	0.99	5.750
0.001	8.5	0.27	1.570	0.85	4.944	0.38	2.210	0.80	4.653
0.001	9.0	0.34	.1.978	0.98	5.700	0.42	2.445	0.90	5.235
0.001	9.5	0.43	2.501	1.17	6.340	0.46	2.675	0.96	5.584
0.001	10.0	0.51	2.966	1,28	7.445	0.46	2.675	1.24	6.049
0.001	10.5	1.04	6.049	1.52	8.841	0.50	2.908	1.15	6.572
0.001	11.0	1.67	9.713	1.96	11.400	0.54	3.141	1.55	9.015

Table 2. Mathematical modeled equations of monovalent ions.

Type of Model	Equation
Linear (L)	$\theta = 2.24\ x_1 + 2.523\ x_2 - 17.71$
Non-Linear (NL)	$\text{Log}\ \theta = 0.1057\ \text{Log}\ x_1 + 2.8852\text{Log}\ x_2 - 1.878$
Non-Linear With Interaction (NLW)	$\theta = 19.109\ x_1 + 3.004\ x_2 - 1.73\ x_1.\ x_2 - 22.395$

Table 3. Mathematical modeled equations of divalent ions.

Type of Model	Equation
Linear (L)	$\theta = -12.3303 + 6.24\ x_1 + 1.86\ x_2$
Non-Linear (NL)	$\text{Log}\ \theta = 0.085303\ \text{Log}\ x_1 + 2.2078\ \text{Log}\ x_2 - 1.20993$
Non-Linear With Interaction (NLW)	$\theta = -6.76 - 13.82\ x_1 + 1.283\ x_2 + 2.057\ x_1.\ x_2$

Table 4. Mathematical modeled equations for combined mono- and divalent ions.

Type of Model	Equation
Linear (L)	$\theta = 3.23933\ x_1 + 2.356\ x_2 - 16.37$
Non-Linear (NL)	$\text{Log}\ \theta = 0.1\ \text{Log}\ x_1 + 2.716\ \text{Log}\ x_2 - 1.71$
Non-Linear With Interaction (NLW)	$\theta = -18.486 + 10.88\ x_1 + 2.574\ x_2 - 0.783\ x_1.\ x_2$

Table 5. Surface charge of anions obtained by potentiometric titration (Bamidele 2003).

Anion	Surface Charge in MicroCoulumbs (μC)			
	1M	0.1M	0.01M	0.001M
NO_3^-	0.79	0.56	0.42	0.22
Cl^-	0.89	0.67	0.65	0.22
Br^-	0.73	0.56	0.56	036
SO_4^{2-}	1.91	1.19	1.12	0.96

Experimental Results and Discussion of Results

Table 5 includes experimental results of the surface charge of anions in MicroCoulumbs (μC) obtained by potentiometric titration (Bamidele 2003) for NO_3^-, Cl^-, Br^- and SO_4^{2-} anions.

Simulated results of the monovalent ions model (NO_3^- Cl^- Br-), the divalent ions model (SO_4^{2-}) and the overall model for NO_3^- Cl^- Br-, and SO_4^{2-} are shown in Table 6.

Comparison of experimental and simulated model results at pH = 9 is shown in Table 7.

The density of MnO_2 was determined to be equal to

(i) Locally made MnO_2 – 240kg/m^3 and
(ii) Refined MnO_2 – 358kg/m^3.

From Table 1, it was observed that at a given concentration the adsorption and also electric surface charge of all the investigated anions increases as pH increases. This is in accordance with Faraday's first law of electrolysis.

This in effect prolongs the life span of the leclanche cell. This is in accordance with the work of Li (Li *et al.* 1996).

Polymath 3 and FORTRAN-77 software programs were used for statistical analysis of the various mathematical models.

From Tables 8, 9, and 10, the significance F for literally all models is within acceptable limits. This means that the variance between the models and the experimental results is low.

Also, for the correlation coefficient for the monovalent ions table, the value for R^2 is highest for the non-linear model. This simply means that the mathematical model of

$$\text{Log}\ \theta = 0.1057\ \text{Log}\ x_1 + 2.8852\ \text{Log}\ x_2 - 1.878$$

from Table 2, best represent the experimental data for these cases.

In the case of the divalent ions, the linear equation from Table 3:

$$\theta = -12.3303 + 2.24\ x_1 - 1.86\ x_2$$

best describe the set of data for it.

Furthermore, for the combined monovalent and divalent ions result, the largest value of R^2 was obtained with the aid of the non-linear equation from Table 4:

Log θ =0.1 Log x_1 + 2.716 Log x_2 - 1.71.

Generally, the highest value of R^2 in the entire model was obtained through the equation from Table 3:

θ = -6.76 – 13.82 x_1 + 1.283 x_2 + 2.057 x_1x_2.

Therefore, it can be said to be the best model for this work. In the case of standard error, the values are lowest in the case of non-linear equations and highest for linear equation. However, in all cases the standard error is still within acceptable limits. The following reasons for error can be given:

(i) Limitation imposed by assumption: this simplifying assumption taken has a consequence on the accuracy of the simulated results.
(ii) Understanding of physical data: this is the possibility that the data used in determining some parameter could contain error e.g. during the calculation of ΔV (change in volume), during interpolation or during calculation of adsorption.

Table 6. Simulated results.

		Monovalent ions model NO_3^- CL^- Br^-			Divalent ions model SO_4^{2-}			Overall Model for NO_3^- Cl^- Br^-, and SO_4^{2-}		
x_1	x_2	L	NL	NLW	L	NL	NLW	L	NL	NLW
1	8.5	0.716	6.359	7.543	9.720	6.951	7.810	6.859	6.521	7.618
1	9.0	7.237	7.499	8.180	10.650	7.886	9.480	8.073	7.616	8.513
1	9.5	8.499	8.765	8.817	11.580	8.886	11.150	9.251	8.821	9.409
1	10.0	9.760	10.162	9.454	12.510	9.951	12.820	10.429	10.139	10.304
1	10.5	11.022	11.699	10.091	13.440	11.083	14.490	11.607	11.576	11.200
1	11.0	12.283	13.379	10.728	14.370	21.282	16.160	12.785	13.135	12.095
0.1	8.5	3.960	4.985	3.579	4.104	5.711	4.512	3.980	5.180	3.815
0.1	9.0	5.221	5.879	4.995	5.034	6.480	5.256	5.158	6.050	5.063
0.1	9.5	6.483	6.871	6.410	5.964	7.301	6.001	6.336	7.006	6.311
0.1	10.0	7.744	7.976	7.826	6.894	8.177	6.745	7.514	8.054	7.559
0.1	10.5	9.006	9.171	9.241	7.824	9.107	7.489	8.692	9.195	8.800
0.1	11.0	10.267	10.489	10.657	8.754	10.092	8.2345	9.870	10.433	10.055
0.01	8.5	3.758	3.908	3.183	3.542	4.693	4.182	3.688	4.114	3.435
0.01	9.0	5.019	4.609	4.676	4.472	5.324	4.834	4.866	4.805	4.718
0.01	9.5	6.281	5.587	6.170	5.402	5.99	5.486	6.044	5.506	6.001
0.01	10.0	7.542	6.246	7.663	6.332	6.718	6.138	7.222	6.397	7.285
0.01	10.5	8.804	7.190	9.156	7.262	7.483	6.789	8.400	7.304	8.568
0.01	11.0	10.065	8.223	10.650	8.192	8.292	7.441	9.758	8.287	9.851
0.001	8.5	3.738	3.064	3.183	3.486	3.856	4.149	3.659	3.268	3.393
0.001	9.0	4.999	3.613	4.645	4.416	4.375	4.759	4.837	3.817	4.684
0.001	9.5	6.261	4.223	6.146	5.346	4.929	5.434	6.015	4.421	5.970
0.001	10,0	7.552	4.893	7.647	6.276	5.520	6.077	7.193	5.082	7.257
0.001	10.5	8.784	5.637	9.148	7.206	6.148	6.719	8.371	5.802	8.544
0.0015	11.0	10.045	6.446	10.649	8.136	6.813	7.362	9.549	6.583	9.830

Table 7. Comparison of experimental and simulated model results at pH = 9.

Con-centra-tion	Experimental				Monovalent Model			Divalent Model			Overall Model		
	$N0_3^-$	Cl^-	Br^-	SO^-_4	L	NL	NLW	L	NL	NLW	L	NL	NLW
1	8.143	6.980	7.561	9.888	7.237	7.499	8.180	10.650	7.886	9.480	8.073	7.616	8.513
0.1	4.362	9.306	5.816	5.816	5.221	5.879	4.990	5.034	6.480	5.256	5.158	6.049	5.063
0.01	5.816	6.689	3.781	5.235	5.019	4.644	4.676	4.472	5.324	4.834	4.866	4.205	4.718
0.001	2.327	2.326	5.816	4.944	4.999	3.613	4.645	4.416	4.375	4.792	4.837	3.817	4.684

Table 8. Statistical analysis of monovalent ions model.

	L	NL	NLW
R^2	0.234154	0.472900	0.250387
Standard Error	4.341144	0.174255	4.326354
Significance *F*	1.00663	2.54278	1.92403

Table 9. Statistical analysis for combined monovalent and divalent ions model.

	L	NL	NLW
R^2	0.289780	0.488925	0.293642
Standard Error	3.859430	0.158949	3.869784
Significance *F*	1.22958	2.78310	4.86527

Table 10. Statistical analysis of divalent ions model.

	L	NL	NLW
R^2	0.886794	0.642661	0.938232
Standard Error	1.166749	0.101544	0.883116
Significance *F*	1.16308	2.02925	2.90575

Conclusion

From simulation results obtained from the mathematical models, the following conclusions can be made:

(i) For all anions, the higher the concentration of the anions and alkalinity of the solution, the greater the surface charge output.

(ii) That the divalent ion (SO_4^{2-}) is preferable when compared with monovalent ions: NO_3^-, CL^-, and Br^-, that the adsorption and hence the surface charge is higher.

(iii) The only SO_4^{2-} has a consistent order of decreasing surface charges from 1M to 0.001M solutions.

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